

HYDROGEL PROCESS - A NOVEL PROCESS FOR LOW TEMPERATURE CLINKERISATION

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ABSTRACT :

The Research & Development Division of the Associated Cement Cos. Ltd., India had pursued a comprehensive programme on bulk usage of fly ash. Considering the chemistry of low lime Class-F Indian Fly ashes, one approach, which was successfully attempted at the author's laboratory, was development of a process route (Hydrogel Process) of clinkerisation based on the fundamental principle of fly ash activation.

The Process involves activation of fly ash with alkali under non-hydrothermal conditions. The activated fly ash is reacted with Hydrated lime/ Limestone in predetermined proportions to produce the calcium silicate / aluminate hydrates gels, which is de-watered, dried and sintered at 800-1350°C to produce the cement clinker. The sintering temperature depends on the type of cementitious system intended (Cementitious binder / Belite rich or Alite rich cement) to be produced. The process makes it possible to use about 20-50 % fly ash.

The authors have also attempted to evolve the possible mechanism of phase formation in the hydrogel process, through studies on microstructure and mineralogy of the calcined material at periodic intervals of temperature.

The paper also illustrates the experimental data generated on the compositional parameters and the compressive strengths of neat cements and its behavior in sulphatic environment for cementitious binder, indicating this cementitious binder to have more sulphate resistance than the conventional Portland cement.

Keywords : Hydrogel, Alkali activated fly ash, Reactivity, Clinkerisation

1.0 INTRODUCTION :

In India approximately 95 million tones per annum of fly ash is generated from the thermal power plants. Disposal/utilization of these fly ashes is a major issue. It is a challenge to the Research Scientists for converting these fly ash into suitable products. The Research and Development Division of The Associated Cement Companies Limited have been pursuing several approaches for converting fly ash to suitable value added products. One of such approaches investigated in detail was conversion of fly ash (Class-F) to cementitious products through Hydrogel Process of clinkerisation ^[1,2]

The Hydrogel is based on alkali activation of the low lime class – F fly ash. The alkali activated fly ash is reacted with hydrated lime (proportion of the hydrated lime depends on the type of cementitious system to be produced) to produce the Hydrogel (a gelated mass produced having calcium silicate and calcium silicate-aluminate hydrates) . The hydrogel on calcination/sintering (temperature dependent on the type of cementitious system to be produced) produces the sinter/

clinker which on inter grinding with gypsum produces the cement/ cementitious binder. The process makes it possible to use about 20-50 % fly ash.

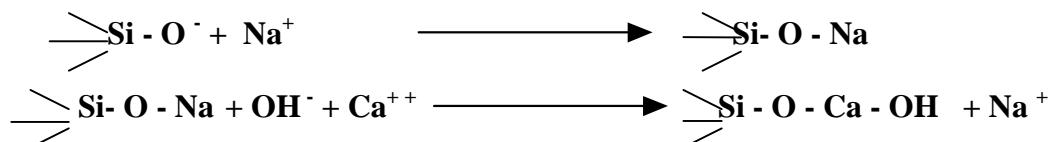
The paper discusses the mechanism of hydrogel process of clinkerisation indicating the observed mineralogical and micro-structural changes in the hydrogel during the thermal processing. The hydrogel compositions can be tailor made to produce either (i) Low temperature Cementitious Binder or (ii) Belite or Alite rich Ordinary Portland cement Clinker.

The paper presents the optimized composition of the hydrogels, temperature of calcination / sintering of these cementitious systems discussing in detail the hydraulic properties of the resultant cements / binder.

1.1 Hydrogel Process – Mechanism:

The possible mechanism ^[3] of hydrogel process is summarised below :

- The alkali reacts with quartz converting to glassy silicates
- Amorphous alumino- silicates of fly ash reacts to form sodium alumino- silicate hydrates
- When the alkali activated fly ash is suspended in water the meta stable glassy phases are partially solubilised thus producing zeolitic hydrophilic sites with Na^+ ions which act as cation exchanger
- On addition of Hydrated Lime The Ca^{++} ion gets exchanged forming Calcium Silicate - Aluminate Hydrates, the sequence of reactions can be represented as:



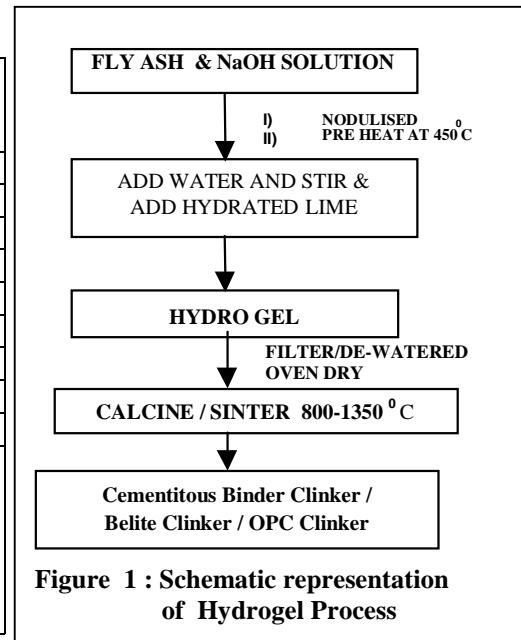
Similar reactions would be expected to occur with the aluminates

The processing steps of the Hydrogel process are schematically represented in Figure 1.

The chemico-mineralogical composition of fly ash and hydrated lime used for Hydrogel preparation is given in Table-1. The mineralogical changes produced in fly ash on activation is shown in Figure 2.

Table-1 : Chemico-mineralogical composition of fly ash and hydrated lime

% Oxides	Fly ash	Alkali Activated Fly ash	Hydrated lime
SiO_2	65.2	63.6	3.0
Al_2O_3	24.8	24.2	1.3
Fe_2O_3	4.8	4.6	1.2
CaO	0.8	0.7	60.4
MgO	0.4	0.3	0.1
LOI	1.4	1.8	33.8
TiO_2	1.4	1.3	-
Na_2O	0.06	2.5	-
K_2O	0.2	0.2	-
Mineralogy	α - Quartz Amorphous phase Mullite Magnetite	α - Quartz Amorphous phase Analcime, Mullite Magnetite	Calcite Calcium hydroxide CaO



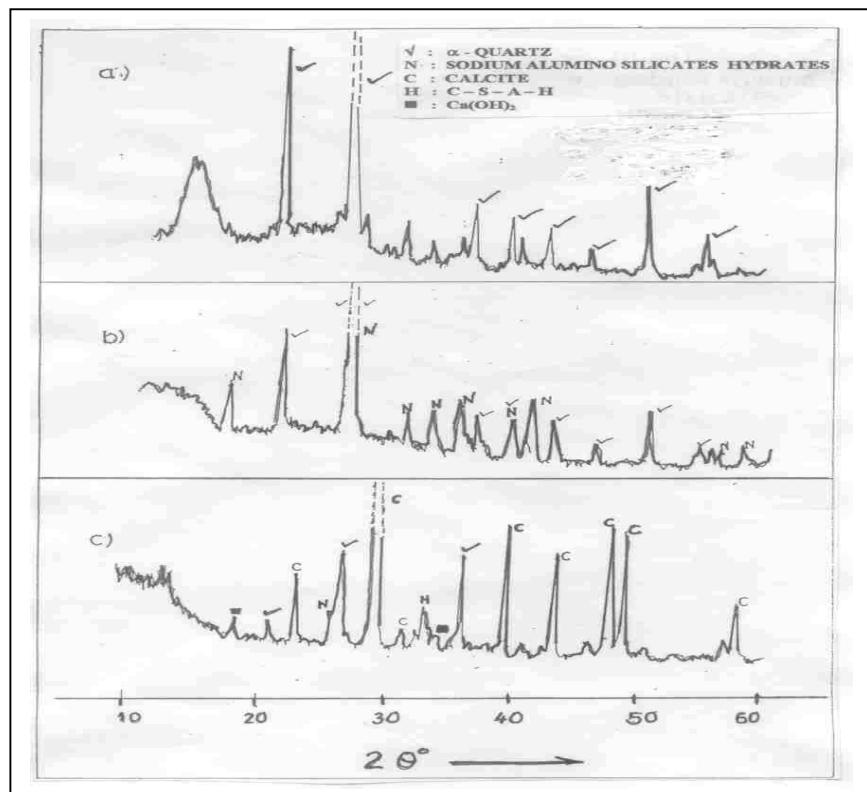


Figure 2: XRD scans of a) Fly ash b) Alkali Activated Fly ash c) Hydrogel

1.2 Mineralogical & Microstructure Characteristics of Hydrogel during Thermal Processing:

1.2.1 dried hydrogel & hydrogel fired at $600^0 C$:

- The content of Calcium - Silicate - Aluminate Hydrates (of Hydroglosular series C_3AH_6 , $C_3AS_2H_2$ etc.) along with it's crystallinity increases as the gel is heated to $600^0 C$
- The calcite /Calcium hydroxide contents decreases

The morphological and microstructural features are similar except that the gel fired at $600^0 C$ shows more extent of interlinking & cross linking with higher compaction of the spherical / aggregated grains of the dried gel (Figure3 a & 3 b) .

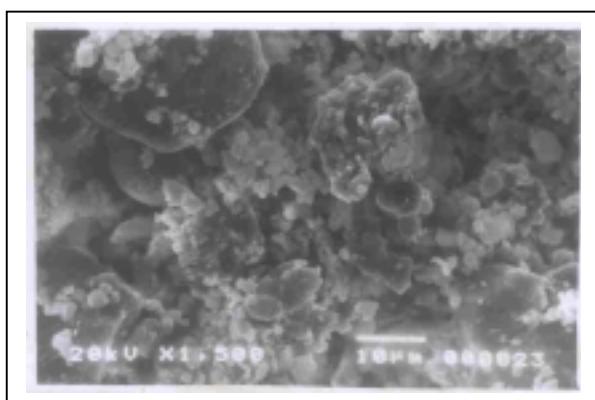


Figure 3 (a) : SEM Photomicrograph of dried Hydrogel

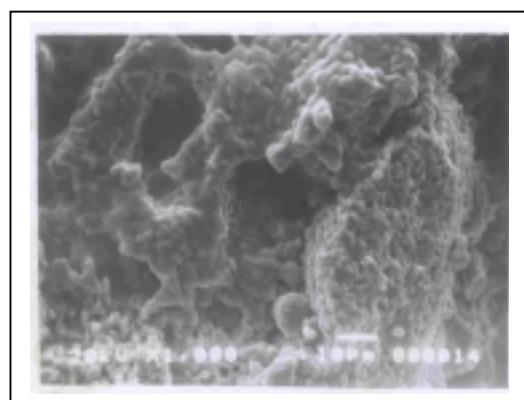


Figure 3 (b) : SEM Photomicrograph of Hydrogel showing Interlinking & Cross linking of spherical grains

1.2.2 hydrogel fired at $700^0 C$ & $800^0 C$:

- The content & crystallinity of the Calcium-Silicate-Aluminate Hydrates (C-S-A-H) increases indicating crystallisation of the Hydrates from its amorphous precursors in Hydrogel
- Further decrease in calcite /Calcium hydroxide contents
- Further inter-linking & cross linking of the spherical / aggregated grains is observed
- Microfine β -C₂S grains are observed which are compacted , inter-linked & crosslinked similar in habit to their (C-S-A-H) precursors (Figure 3 c)

The changes up to $800^0 C$ are in hydrogel compositions for Low temperature Cementitious Binder system. The thermal changes in hydrogel compositions for Belite rich and alite rich Ordinary Portland Cement clinker are summarised below :

1.2.3 hydrogel fired at $900^0 C$ & $1000^0 C$:

- The calcium - silicate -Aluminate Hydrates (C-S-A-H) decreases from $900^0 C$ to $1000^0 C$, till at $1000^0 C$ it is absent. This disappearance of the hydrates is also substantiated by the loss observed at $900 - 950^0 C$
- Appearance of C₂S & C₂AS phases at $900^0 C$ and increase in their contents at $1000^0 C$

1.2.4 hydrogel fired at $1100^0 C$ & $1200^0 C$:

- The C₂AS phase decreases from $1100^0 C$ to $1200^0 C$ till $1200^0 C$ it is absent.
- Presence of C₃S & C₃A is observed along with an increased C₂S contents at $1100^0 C$
- At $1200^0 C$ the microstructure depicts well formed clinker phases.

1.2.5 hydrogel fired at $1300^0 C$ & $1350^0 C$:

- Further increase in phase formation (C₃S and C₃A) (Figure3 d)
- At $1350^0 C$ the clinker shows well crystallized cement clinker phases with α 'form of belite, the aluminates are coarse crystallized lathic in shape. The clinker is observed to be porous.

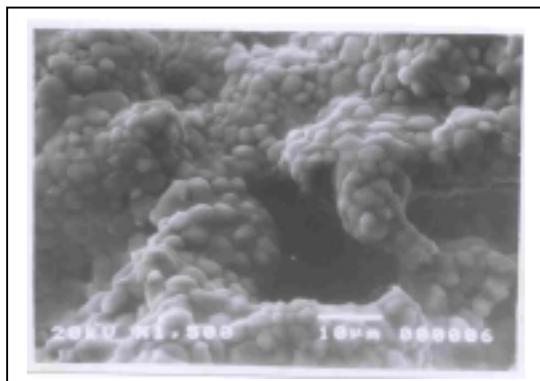


Figure 3 (c) : SEM Photomicrograph of microfine β -C₂S grains

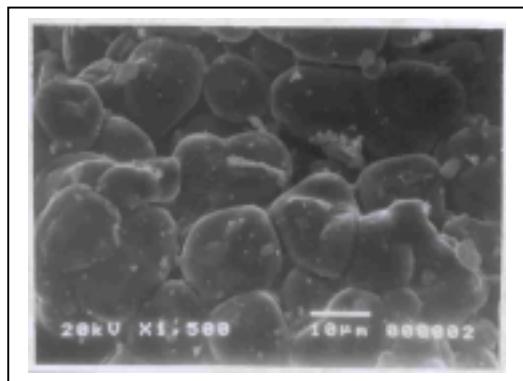


Figure 3 (d) : SEM Photomicrograph of well formed Clinker phases

The mineralogical changes during the thermal processing are summarised in Figure . 4

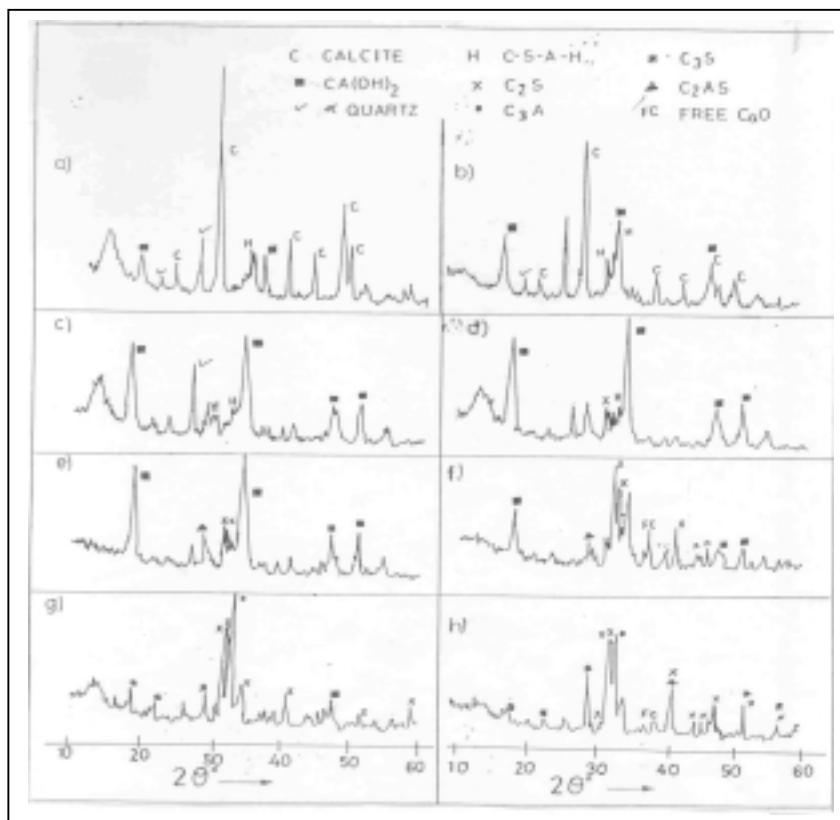


Figure 4 : XRD Scans of Hydrogel fired at different temperatures

a) 600°C b) 700°C c) 800°C d) 900°C
 e) 1000°C f) 1100°C g) 1200°C h) 1350°C

2.0 MANUFACTURE OF BELITE AND ALITE RICH OPC CLINKERS

The proportions of the activated fly ashes and hydrated lime along with chemical composition of the corresponding Hydrogels and resultant clinkers is given in Table - 2 &3

Table – 2 : Raw material proportions and gel compositions

	Hydrogel Clinker I mix	Hydrogel Clinker II mix
Raw material proportions		
Activated fly ash	23.5	--
Activated flyash + Siliceous corrective		20.7
Hydrated lime	76.5	79.3
Chemical Composition		
% Oxides		
SiO ₂	17.2	16.58
Al ₂ O ₃	6.68	4.35
Fe ₂ O ₃	2.02	2.96
CaO	46.14	48.01
MgO	0.17	0.13
LOI	26.19	27.11
Na ₂ O	0.61	0.34
Modulii Conditions		
LSF	0.80	0.90
SM	1.98	2.27
AM	3.3	1.47

**Table – 3 : Chemical Composition
of Clinkers**

% Oxides	Clinker - I	Clinker - II
SiO ₂	23.36	22.75
Al ₂ O ₃	9.05	5.97
Fe ₂ O ₃	2.74	4.07
CaO	62.51	65.87
MgO	0.23	0.20
Na ₂ O	0.83	0.47
Free CaO	1.0	1.0
Modulii Conditions		
LSF	0.80	0.90
SM	1.98	2.27
AM	3.3	1.47
Potential phase composition		
C ₃ S	8.1	45.2
C ₂ S	60.9	31.2
C ₃ A	19.4	8.9
C ₄ AF	8.3	12.4
C/S Ratio	2.68	2.9

2.1 Reactivity and phase formation during sintering :

The reactivity (lime combining ability) of the hydrogel at different temperature was compared with raw mix prepared from fly ash (unactivated) and hydrated lime. The two mixes were fired at different temperature from 600 - 1350°C at intervals of 100 °C and a retention time of 20 min at each temperature. The fired samples at each temperature were analysed for free lime to assess the degree of reaction. The plot of free CaO v/s temperature of the mixes is shown in Figure 5 . The results indicate a substantial improved reactivity of the hydrogel compositions.

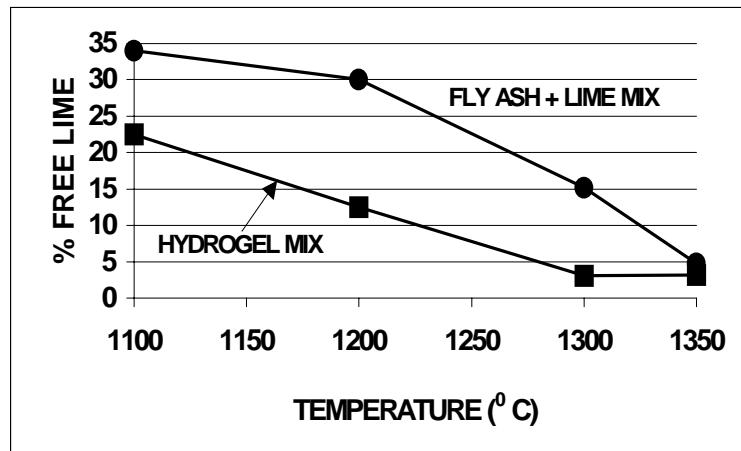


Figure 5 : Comparative Reactivity of Hydrogel Mix and Fly Ash +Lime Mix

2.2 Preparation and Charaterisation of clinkers:

Using Hydrogel process Clinkers were produced at pilot scale level. The optimum compositional parameters of the alite rich and belite rich clinkers are as follows:

	LSF	SM	AM	POTENTIAL PHASES			
				C ₃ S	C ₂ S	C ₃ A	C ₄ AF
CLINKER – I (Belite Clinker)	0.80	1.98	3.3	8.1	60.9	19.4	8.3
CLINKER – II (Alite rich Clinker)	0.90	2.27	1.47	45.2	31.2	8.9	12.4

Clinker – I (Belite Clinker) and Clinker – II (Alite rich Clinker) were prepared from the hydrogel prepared from alkali activated fly ash. The microstructure of the clinkers is presented in Figure 6 a & b).

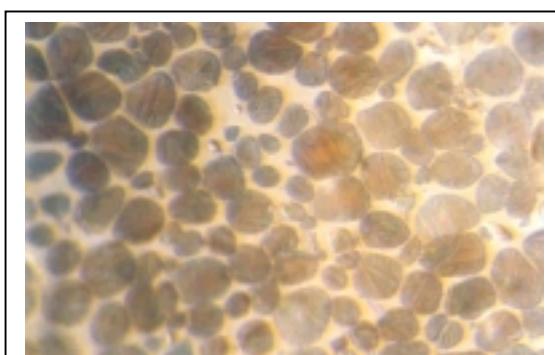


Figure 6 (a) : Photomicrograph of Clinker – I showing well developed C₂S

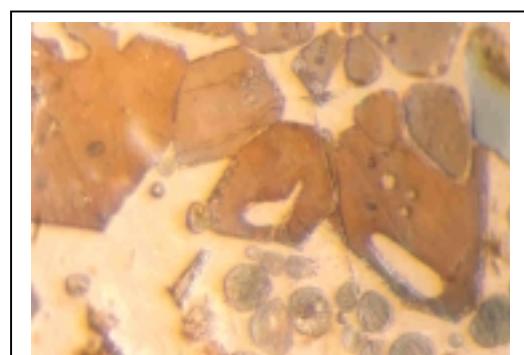


Figure 6 (b) : SEM Photomicrograph of Clinker-II showing well developed C₃S

The clinkers were co-ground with gypsum in laboratory ball mill to cements with a fineness of 320 m^2/Kg and SO_3 content of 2.7%. The physical properties of cements are given in Table : 4

Table – 4 : Physical Properties Of Cements (Indian Standards)

Physical tests	Belite rich Cement	Alite rich Cement
Blaine's Specific surface (m^2/Kg)	320	320
SO_3 (%)	2.7	2.6
Consistency (%)	28.3	25.6
Setting Time(mins.)		
Initial	75	110
Final	115	165
Compressive strengths (MPa)		
1 Day	11.0	24.5
3 Days	16.0	42.0
7 Days	22.0	58.5
28 Days	33.0	79.5

3.0 MANUFACTURE OF LOW TEMPERATURE CEMENTITIOUS BINDER(CB) :

The raw materials used for the study were having same composition as given in Table –1. The detail investigation is reported in ^[4] and the optimum clinker (chemical and mineralogical) composition of hydrogel sintered at 800 $^{\circ}\text{C}$ is shown in Table-5, whereas SEM photomicrograph of clinker in Figure 7 and compressive strength of neat cement paste with optimum gypsum is shown in Figure 8.

Table-5 : Chemical and Mineralogical Composition of Optimum low temperature belite Clinker (on loss free basis)

% Oxides	Clinker
SiO_2	32.51
Al_2O_3	16.74
Fe_2O_3	2.78
CaO	45.15
MgO	0.63
Na_2O	0.04
K_2O	0.55
SO_3	0.11
CaO/SiO_2	1.39
Mineralogical Composition	C_2S , C_3A , α -Quartz, f CaO , $\text{Ca}(\text{OH})_2$

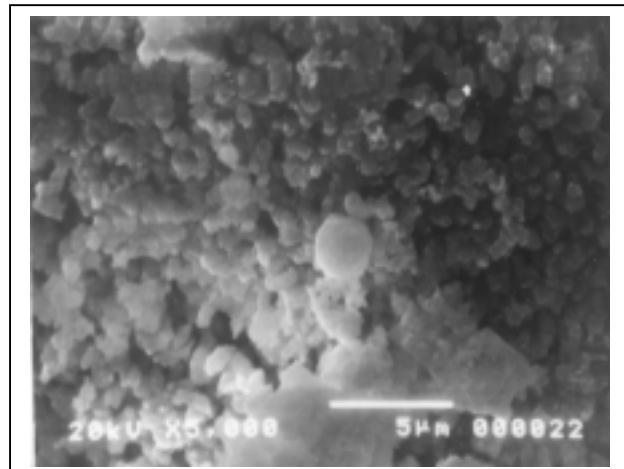


Figure 7. : Hydrogel at 800 $^{\circ}\text{C}$ showing microfine β - C_2S

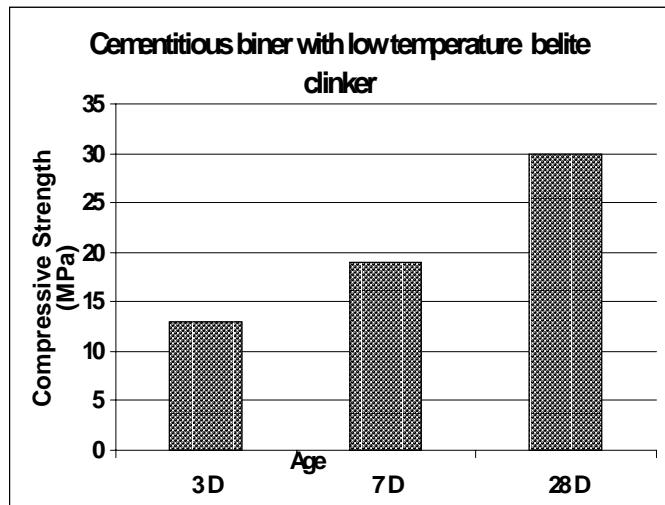


Figure 8 : Compressive strength of low temperature belite clinker

3.1 Effect of Aggressive Environment on the Cementitious Binder^[4,5] :

Mortars prisms were cast with Cementitious binder and were cured by immersing in the aggressive solution (0.5M Na_2SO_4 + 0.5 M NaCl solution) after 2 days of hydration in de-mineralised water, after 3, 7 & 28 days of hydration they were tested for compressive strengths and flexural strengths.

- X-ray diffraction analysis by Philips X'pert MPD
- Chloride and sulphate content of the Outer coat and inner cores of the prisms were analysed by conventional methods.

- SEM analysis of the fractured surface of the mortar prisms cured at 28-days in water and in aggressive environments was carried out on Jeol JSM 5400.
- Pore size distribution of the hydrated mortar cubes cured at 28-Days in water and the aggressive environment was determined by Hg porosimeter.

3.1.1 effect of sulphate + chloride solution on cementitious binder mortar :

The Flexural and compressive strengths of the mortars cured in de-mineralised water and the aggressive environment are graphically shown in Fig 9 & 10

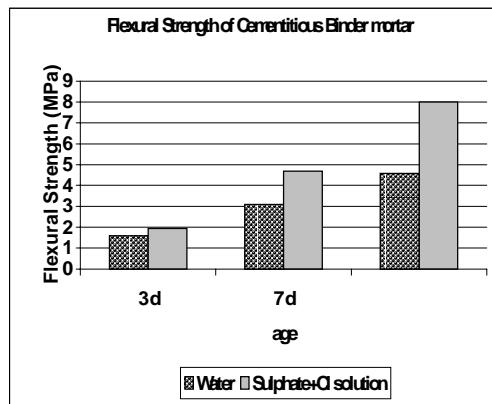


Figure 9 : Flexural strength of Cementitious Binder mortar in water & aggressive environment

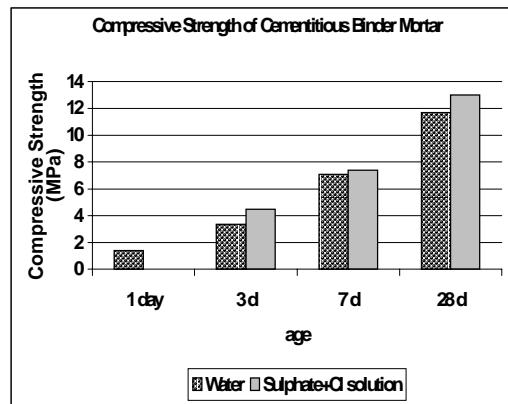


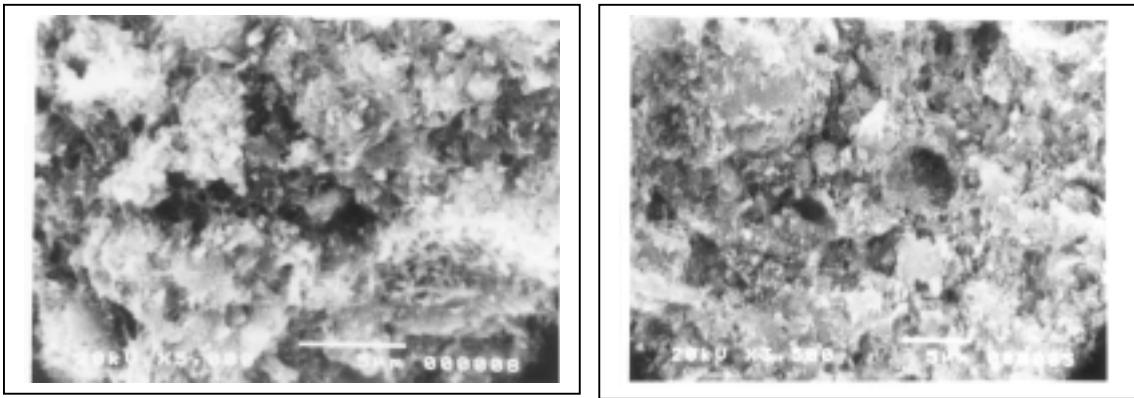
Figure 10 : Compressive strength of Cementitious Binder mortar in water & aggressive environment

The outer coat of prisms were cut at a distance of 1 cm along all the faces and the averaged outer coat along with the central core was tested for sulphate and chloride concentration and compared with that of the prisms cured in de-mineralised water. The results are tabulated in Table - 6 .

Table- 6 : Sulphate and chloride content of the mortar prisms

	3 days Hydration		7 days Hydration		28 - days Hydration	
	In Aggr. environment		In Aggr. environment		In Aggr. environment	
	% SO ₃	% Cl	% SO ₃	% Cl	% SO ₃	% Cl
Av. External Coat of all faces of the prism	1.5	0.09	1.5	0.10	1.5	0.09
Core	1.7	0.06	1.6	0.08	1.6	0.06

The SEM photomicrographs showing the hydrated microstructure^(6,7) of the mortars cured in water and in aggressive environment at 28- Days are shown in Figure 11 (a & b).



(a) Cured in de-mineralized water (b) Cured in aggressive medium
 Figure 11 : Microstructure of the Cementitious binder mortars cured in water and in aggressive medium showing compacted microstructure

The studies indicate that

- Considering the sulphate contents of the cement in the mortars the SO_3 contents of the mortars is marginally more and it increases with age of hydration in the aggressive medium .The chloride levels in mortars are more or less constant with age of hydration indicating that the diffused chloride in the pore solution is in equilibrium with the curing solution and with age the penetration of chloride seems to have been hindered indicated by precipitation of traces of chloride based compounds in pores at 28-days.
- The XRD of the cementitious binder clinker shows amorphous contents along with $\text{C}_2\text{S}, \text{C}_3\text{A}$, calcium hydroxide, calcite and α -quartz, hydrated mortars in water shows formation of Ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3,(\text{OH})_{12}.26.\text{H}_2\text{O}$,Hillbrandite(C-S-H) and Hydroglossular $\text{Ca}_6\text{Al}_2(\text{SiO}_4,\text{CO}_3,\text{OH})_3$ with lesser intensities while in aggressive medium the mortars show much higher levels of these phases along with traces of Hydrocalumite ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2.10\text{H}_2\text{O}$)
- Due to interaction of the water soluble sulphate from the aggressive medium in presence of sodium ions present in the cementitious binder, there is gradual increase in the compaction i.e. decrease in the porosity of the mortar prisms from 7-Day to 28-days, this is attributed to the accelerated formation of Ettringite $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3,(\text{OH})_{12}.26.\text{H}_2\text{O}$.and Hydroglossular $\text{Ca}_6\text{Al}_2(\text{SiO}_4,\text{CO}_3,\text{OH})_3$ and Gismondite $\text{CaAl}_2\text{Si}_2\text{O}_8.4\text{H}_2\text{O}$ and the subsequent precipitation of the

phases inside the pores. Such increased phase formation is not observed in the mortar prisms cured in water and so the porosity is observed to be high..(Figure 11,a & b).

- The flexural strengths of the mortar prisms in aggressive medium shows a substantial increase from 3-Day to 7-Day and to 28-days as compared to those cured in water.
- The porosity of the mortars at 28-days of hydration in aggressive medium is much less, it was observed to have lower porosity in the range of micro pores as compared to those cured in water. (Figure 12)

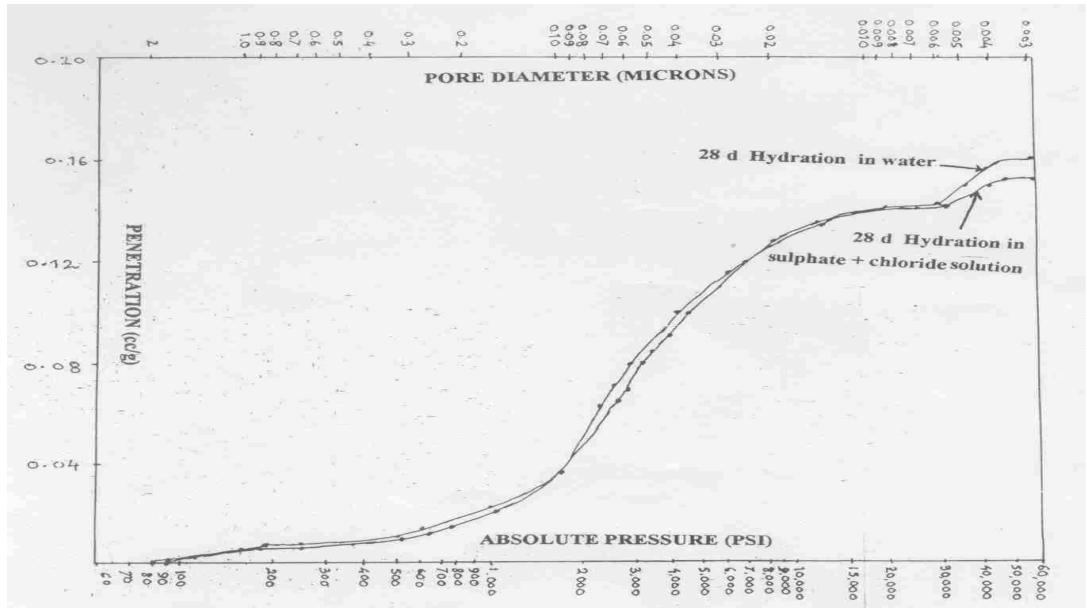


Figure12 : Pore size Distribution of cementitious binder mortars cured in water and in aggressive medium

CONCLUSIONS:

- The Hydro gel process of clinkerisation utilises fly ash up to 50% and opens new avenue for it's utilization. The optimum alkali levels required for activation being dependent on the nature of fly ash. The process does not involve hydrothermal activation.
- Depending upon type of Cementitious system intended to be produced viz. Cementitious binder clinker / belite rich or alite rich clinker. The temperature for thermal processing ranges from 800 -1350°C.
- The study establishes the possible mechanism of Hydrogel process. Alkali activation of fly ash produces sodium alumino silicate hydrates, these zeolitic structures with hydrophilic sites act as cation exchangers exchanging the alkali ion with the Calcium ion, thus forming calcium-alumino silicate hydrates. These semi amorphous precursors present in the hydrogel dehydrate to produce the cement clinker minerals.
- The principle of alkali activation can be extended to activation of white china clay for manufacture of white cement, initial experiments have indicated the feasibility of white cement manufacture at lower temperature using this hydrogel process.
- The resistance of cementitious binder to aggressive environment is excellent. Such a binder could have specialised applications.

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